Carbon Dioxide (CO_2) Adsorption in MOF-5

By

Nur Hazirah binti Shafii

(14297)

Dissertation submitted in partial fulfilment for

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

JANUARY 2014

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Carbon Dioxide (CO_2) Adsorption in MOF-5

By

Nur Hazirah binti Shafii

A project dissertation submitted to the

Chemical Engineering Programme

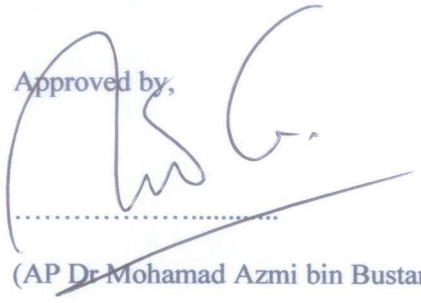
Universiti Teknologi PETRONAS

In partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,



.....

(AP Dr Mohamad Azmi bin Bustam@Khalil)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own excepts as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

.....

NUR HAZIRAH BINTI SHAFII

ABSTRACT

Metal-organic Frameworks (MOFs) materials are the compounds consist of metal ions or clusters coordinated to often rigid organic molecule, forming one-, two-, or three-dimensional structures that can be porous. It is one of carbon dioxide (CO_2) Capture and Storage (CCS) which has been used mostly for separation of gas such as, separating CO_2 from the natural gas and also to reduce the anthropogenic emission of CO_2 to the atmosphere. These porous network structures show a great potential compared to monoethanol amine (MEA). One of the most studied MOFs is MOF-5 due to its high surface area, flexible structure, attraction to certain gases and cheap raw materials. Since most of the experiments are studied on hydrogen (H_2) adsorption, this project is conducted with the aims to study on how much CO_2 can be adsorbed/separated by MOF-5 and MOF-5 modified with multi wall carbon nanotubes (MWCNTs) and expandable graphite (EG) at the temperature of 298.15 K as well as to examine whether the modified MOF-5 can improve the adsorption of CO_2. MOF-5, MWCNTs@MOF-5 and EG@MOF-5 were synthesized, characterized and then, used as the samples in the CO_2 adsorption experiment according to the objective of this project. The result shows that the modified MOF-5 can enhance the CO_2 storage compared to the pure MOF-5.

ACKNOWLEDGEMENT

The past 28 weeks of my enrolment in this final year project have been truly a valuable experience to me. Therefore, I would like to take this opportunity to express my gratitude to a number of people that have helped me throughout this project.

First and foremost, all praises to the Almighty, Allah S.W.T. for His mercy and grace, I was able to complete this project in good health and well being. Next, I would like to sincerely thank you my Supervisor, AP. Dr. Mohamad Azmi bin Bustam@Khalil who has supervised me throughout my project period. His willingness to guide and advice me had helped me in achieving the goals of my project. Besides, he was constantly supportive of the decisions that I make and always share his knowledge and experiences with me.

On the other hand, I would like to extend my gratitude and appreciation to the postgraduates, Dr Sami Ullah and Dr Ali who had guided and taught me in many things throughout my final year project. Without their guidance, it is impossible for me to finish the final year project within the given period.

Very special thanks to both of my parents and family for their love and supports. Last but not least, thanks to my colleagues, friends and those who involved directly and indirectly towards accomplishing my final year project's objectives. In short, I feel blessed to have successfully completed my final year project and for all help that the aforementioned parties have given me. My final year project only becomes a success with their help.

Thank you.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLE

ABBREVIATIONS AND NOMENCLATURES

BDC	1,4-benzenedicarboxylate
BET	Brunauer-Emmet-Teller
CCS	carbon dioxide capture and storage
CH_4	methane
CO_2	carbon dioxide
DMF	dimethyl formamide
EG	expandable graphite
FESEM	field emission scanning electron microscopy
FYP	final year project
H_2	hydrogen
MOF	metal organic framework
MWCNTs	multi wall carbon nanotubes
TGA	thermal gravimetric analysis
TEM	transmission electron microscopy
XRD	powder x-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

The anthropogenic emission of CO_2 gas has been increased drastically and caused climate change on the earth. According to Zhonghua, Sanhua and Dapeng (2012), compared to a thousand years ago, the concentration of CO_2 has been increased by 36% increment which is about 260 to 355 ppm.

Figure 1 shows the increased of CO_2 in the atmosphere from 1960 to 2010 and keep on increasing until today (Li et al., 2011). CCS technologies are being used in order to reduce the CO_2 concentration in the atmosphere. Furthermore, it is also being used to separate CO_2 from other gases to get a purify one for example, removing CO_2 from the natural gas.

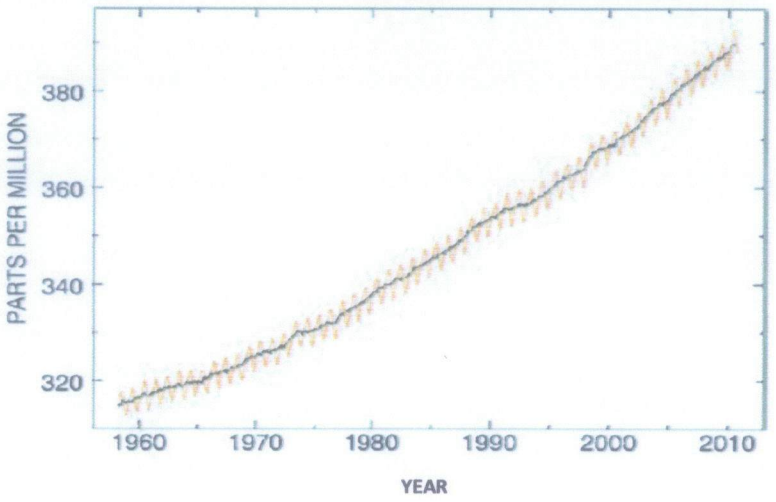


Figure 1: Atmospheric CO_2 concentration from 1960 to 2010.

The U.S. Energy Information Agency states that the production of natural gas is the second largest source of CO_2 emissions in the United States (US) where the largest source of CO_2 emissions is the actual combustion of coal, oil and natural gas to be use in energy and transportation applications (Sciences, 2012). The most expensive

step in biofuel upgrading is the removal of CO_2 from raw products in order to purify biogas. Removing CO_2 from natural gas is also important to help the pipeline from undergo corrosion where the CO_2 concentration needs to be as low as 2% (Mu, Schoenecker, & Walton, 2010).

Metal–organic frameworks (MOFs) are considered among the leading candidates for CO_2 removal from power plant fumes as many nations already started cutting their emissions through renewed regulations (Jung et al., 2013). Crystalline MOFs exhibiting low density structures, high surface areas, and tunable structures create a center of attention much attention because of their potential applications in hydrogen storage, CO_2 adsorption, and catalysis (Zhang & Hu, 2011). MOF-5 is one of the most studied MOFs because it has high surface area, cheap raw materials, easy to be synthesis, thermal stability and it consists of mostly fresh air where 60% of the volume is accessible to the guests (Telfer, 2010).

1.2 Problem Statement

MOF-5 is one of the most potential MOFs as it has high surface area and thermal stability. Furthermore, the raw materials needed to synthesize it are easy to get and the crystal can be synthesized easily compared to other MOFs. Previous researches mostly studied on hydrogen and methane adsorption, specifically, there are not many researches made about CO_2 adsorption in MOF-5 in terms of the comparison with MOF-5 modified using multi wall carbon nanotubes (MWCNTs) and expandable graphite (EG). Therefore, this project is done by studying the CO_2 adsorption in MOF-5 at the temperature of 298.15 K and pressure of 1 atm.

1.3 Objectives and Scope of Study

The main objectives for this project are;

1. To synthesis and characterize MOF-5 and MOF-5 modified with MWCNTs and EG.
2. To study CO_2 adsorption into MOF-5, MWCNTs@ MOF-5 and EG@ MOF-5 at the temperature of 298.15 K and pressure of 1 atm.

This project involved the synthesis of samples, characterization of samples and a CO_2 adsorption experiment. In addition, the synthesis and adsorption experiment were conducted in CO_2 laboratory while the characterization was done by the authorized personnel.

1.4 The Relevancy of the Project

This project is relevant to the industrial plants nowadays that having problem in removing or separating CO_2 as the quantity of CO_2 keep on increasing in the atmosphere. Many researches have been done to find the best method and varied the current methods to remove or capture the CO_2. MOF-5 is one of the potential carbon dioxide capture and storage and still being under researches in modifying the structure to give the optimum CO_2 adsorption.

1.5 Feasibility of the Project within the Scope and Time Frame

The time frame that are allocated for this project is basically enough to do the synthesis, characterization and also adsorption experiment. The time allocated for the project is almost three months for FYP I and three months for FYP 2. For the experiments that are required to be done, it takes approximately three months to finish it up and thus it is possible to do within the time allocated.

CHAPTER 2

LITERATURE REVIEWS/THEORY

2.1 CO_2 Capture and Storage

In order to reduce the emission of CO_2 to the atmosphere, CO_2 capture and storage (CCS) have been used. Capture of CO_2 is only feasible for large point sources for instance, fossil-fuel based power plants and large industrial installation, due to practical and economic reasons. Usually, post-combustion, pre-combustion and oxy-fuel combustion are the three main categories of CO_2 capture technologies (Foundation, 2007). Post-combustion is the CO_2 end-of-pipe separation from the flue gas mostly consist of N_2 and CO_2. Before the absorbent is brought into contact with the flue gas, it is cooled down first. Then, CO_2 will be attached to the absorbent. In the second process, to release concentrated CO_2 and regenerate the absorbent, the liquid solution is heated. Roughly, 80 to 90 percent of the CO_2 can be captured by using this technology (Foundation, 2007).

Pre-combustion capture generates H_2 by producing a reaction of a primary fuel with air or oxygen. The fuel is converted to hydrogen (H_2) and carbon monoxide (CO) and further reaction of CO gas and steam gives more CO_2 and H_2. Lastly, the H_2 and CO_2 gas is separated. The advantage of pre-combustion is it requires lower energy (Li et al., 2011). Oxy-fuel combustion has the severe requirement of nearly pure oxygen, in stead of air. The advantage is that the gaseous product is almost pure CO_2 and can be directly stored. However, the process requires pure oxygen that can be obtained by the separation of air or by other techniques available which might give high capital cost.

Figure 2 shows different technologies and associated materials for CO_2 separation and capture (Li et al., 2011). Capturing CO_2 by porous material is an alternative approach among the CCS technologies due to its energetic efficiency and technical feasibility. Metal-organic frameworks (MOFs) have shown greater potential rather than other CCS technologies as they have high specific surface areas (SSAs), pore volume and tuneable pore size.

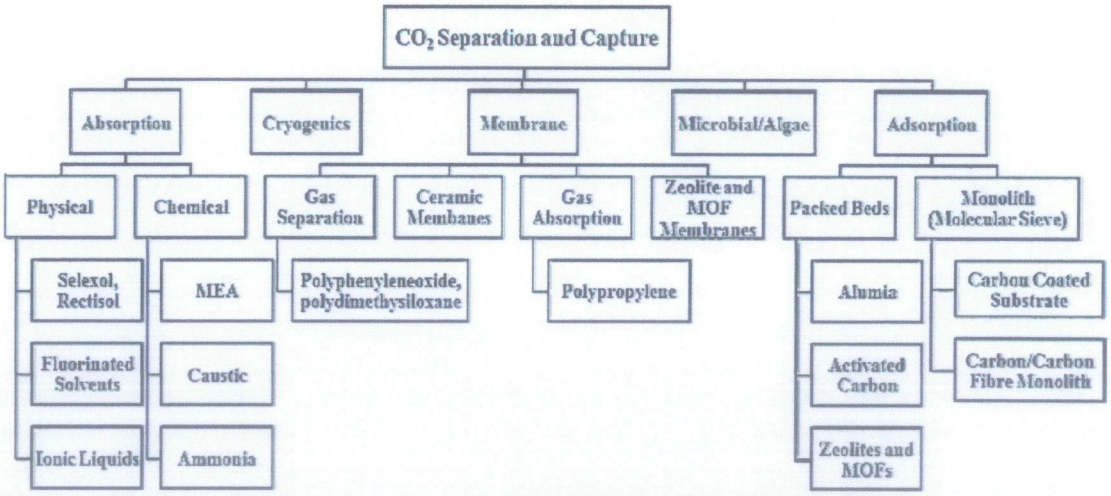


Figure 2: Types of CO_2 Capture and Storage

2.2 Adsorption of CO_2 Using MOFs

Metal-organic frameworks (MOFs) are a class of crystalline porous materials which has been emerged in the past two decades. According to Stephen Caskey, MOFs consist of metal ions or clusters, containing nodes linked by multidirectional organic linkers/ligands and assembled through strong coordination bonds in the network structure. The network can be 1-D, 2-D and 3-D extended, periodic structures (Caskey, 2009). The structure of MOFs could easily be tuned and modified using a building-block approach thus resulting in porous material with high surface area and low-density (Jung et al., 2013). They have a great potential in advancing a variety of applications such as gas storage, adsorption separation, catalysis and gas sensing (Mu et al., 2010).

Basically, MOFs have been studied widely for three main reasons. First and foremost, these materials possess high surface areas, for instance, MOF-177 = 4500m^2/g (Chae et al., 2004), MOF-5 = 3000m^2/g (Eddaoudi et al., 2002), (Yaghi, Rosi, et al., 2003) and Cu-MOF = 3200m^2/g (Seki, 2001) and controlled porosity. It makes them good candidates for gas storage and catalysis. Figure 3 shows the typical surface areas for different materials and MOFs has the highest surface areas compared to zeolites and mesoporous material (Yaghi). Secondly, some MOFs may have attraction for certain gases and, therefore, MOFs could be used in gas separation. For example, Seki's Cu-MOF that has a methane sorption capacity of 212 cm^3 STP g^{-1}, which is superior to the sorption capacity of zeolite 5A and nearly the same as activated carbon AX-21 (Seki, 2001). Third, in terms of chemical composition, MOFs are highly flexible. Thus, it allows the addition of functional groups which could change the pore size and chemical properties of the MOF (Perez, Balkus, Ferraris, & Musselman, 2009).

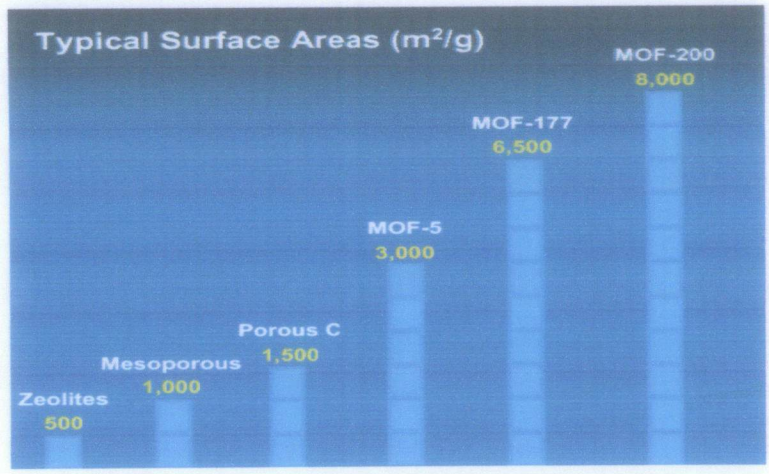


Figure 3: Typical surface areas for different MOFs

There are two types of MOFs which are rigid and flexibility/dynamics. Rigid MOFs generally have comparatively stable and robust porous frameworks. The porous frameworks have permanent porosity. For flexible MOFs, have dynamic and "soft" frameworks which respond to external stimuli, for example, temperature, pressure and guest molecules (Li et al., 2011). Due to their adjustable pore sizes, controllable pore surface properties, and large surface areas, MOFs are the ideal adsorbents or

membrane materials for gas storage and separation. Most MOFs have higher pore volumes and surface areas than other porous material, such as zeolites and activated carbon. The total pore volume of MOFs is proportional to the amount of adsorbed CO_2 at high pressure. In addition, Figure 4 shows that the surface area is strongly connected with the CO_2 storage ability (Li et al., 2011).

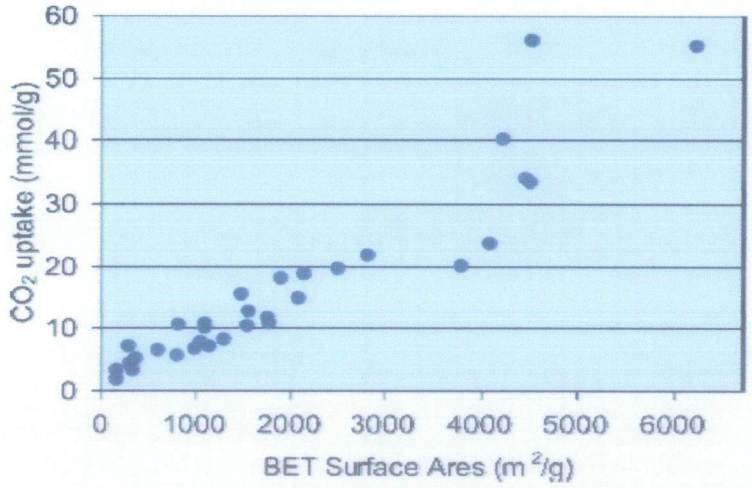


Figure 4: CO_2 uptake vs surface area in selected MOFs (at ambient temperature and high pressure)

A study has been made on a series of 10 MOFs at room temperature and the highest adsorption capacity of CO_2 is 34 mmol/g at 40 bar by MOF-177. Other studies on different materials by using grand canonical Monte Carlo (GCMC) simulations found that IRMOF-16 has the highest capacity of 64 mmol/g at 50 bar (Mu et al., 2010). However, according to Li et al., the highest record for any crystalline material that has been reported to hold the most CO_2 storage record is MOF-210 with the saturated CO_2 uptake of 2400 mg/g at room temperature and pressure of 50 bar. Approximately, MOF-210 has a bulk density of 0.25 g/cm^3, measured pore volume of 3.60 cm^3/g, and a Brunauer-Emmet-Teller (BET) surface area of 6240 m^2/g.

Some studies have been made to study on limited adsorption selectivities of CO_2 over other gases in MOFs which was evaluated from experiments. Deng et al. reported the adsorption equilibrium selectivity of CO_2 over N_2 and CH_4 in MOF-5

and MOF-177, which were calculated from the ratio of Henry's constants (Saha, Bao, Jia, & Deng, 2010). The results showed that the selectivity of CO_2 over N_2 is 17.48 and 17.73 for MOF-5 and MOF-177, respectively, which are lower than that of Zeolite 5A. Meanwhile, the selectivities for CO_2 over CH_4 are 15.53 for MOF-5 and 4.43 for MOF-177 (Li et al., 2011).

2.3 MOF-5

MOF-5 is one of the most relevant MOF members. MOF-5 consists of Zn_4O units connected by linear 1,4-benzenedicarboxylate (BDC), a bi-dentate ligand/linker forming a cubic three dimensional structure with a pore size of 8Å (Perez et al., 2009). In Figure 5, the structure shows that the nodes of the net are built up by Zn containing clusters that work as an octahedral secondary-building unit (SBU), while the spacers are the bi-dentate organic ligands. The carboxylate groups are shared by the two SBUs. MOF-5 is also known as IRMOF-1 because it is the first member of a series of isoreticular metal–organic frameworks. The BDC molecule is replaced by a different spacer. It preserves the topology of the net, providing an elegant way to adjust the pore size and framework functionality (Civalleri, Napoli, Noel, Roetti, & Dovesi, 2006).

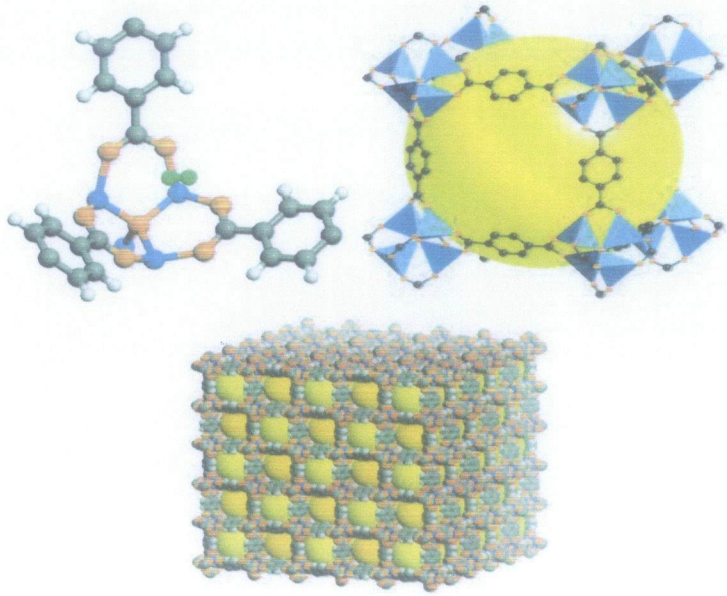


Figure 5: MOF-5 structure where blue = Zn, red = O, black = C and green = H_2 (Yaghi, O'Keeffe, et al., 2003).

MOF-5 has high BET surface area which can go up to 3500 m^2 g^{-1} and a pore volume of 1.31 cm^3 (Jung et al., 2013). MOF-5 nanocrystals possess high thermal stability (up to 400°C) which expands the use of MOF-5 in membrane fabrication (Perez et al., 2009). MOF-5 has been the main subject of a number of papers which mostly studied on its adsorption capacity for gas storage, notably of methane, CO_2 and hydrogen (Civalleri et al., 2006). The first report of MOF-5 written by Omar Yaghi's group in 1999 has made a significant splash where the original paper has been cited for 1400 times in ten years since the publication (Telfer, 2010). According to Yaghi et al., the adsorption value of CO_2 is 22 mmol g^{-1} at 298 K and 40 bar for MOF-5.

Another analysis has been performed by Simmons et al. at different temperatures with a range from 220 K to 310 K and the pressures are up to 32 bars. The highest CO_2 capacity from the analysis is 31 mmol g^{-1} at 220 K. MOF-5 can undergo all tested pressures from 0 to 225 bar without losing its structural integrity. Nevertheless, for an efficient CO_2 capture, one has to stay within the suggested stability window of 3.5 hours of exposure to moist air (at 21.6°C and 49% humidity) in order to avoid structural collapse for reliable gas storage operations (Jung et al., 2013).

Figure 6 shows the results from the experiment for CO_2 adsorption in MOF-5 compared with two simulation models at 298 K (Walton et al., 2007). In the first model (red colour), only Lennard-Jones interactions are considered where the quadrupole moment of CO_2 was ignored. The prediction of this model is the saturation loadings are clearly lower than the one from experiment. The predicted isotherm also does not possess the inflection point seen in the experimental isotherm. For the second model which includes both Lennard- Jones and Coulombic interactions give prediction of better agreement for the saturation loading compared to experiment (Walton et al., 2007).

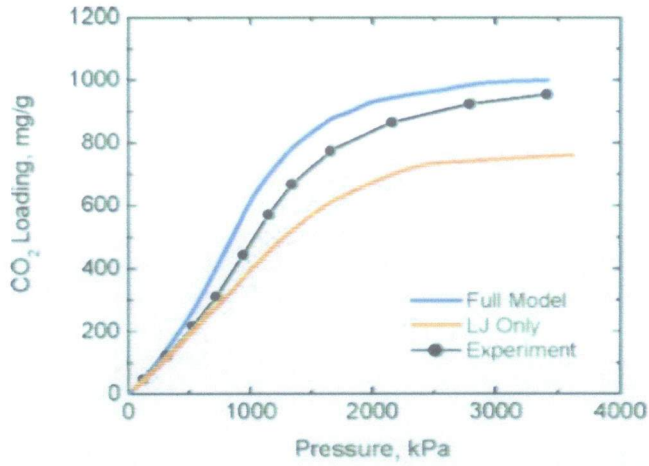


Figure 6: Comparison of experimental adsorption isotherms and GCMC simulations for CO_2 in MOF-5 at 298 K. The blue curve was calculated from a model that included electrostatic effects while the red curve was calculated by considering only the Lennard-Jones interactions

Figure 7 illustrates the carbon dioxide storage by using different MOFs at room temperature (Yaghi). From the graph, MOF-5 or also known as IRMOF-1 is the second MOF that can store highest number of CO_2. Therefore, it is proven that MOF-5 is one of the potential MOFs to be use commercially as CO_2 Capture Storage. Meanwhile, Figure 8 shows the adsorption of CO_2 in MOF-5 at different temperature. From the graphs, it can be concluded that the adsorption will increase when the temperature decreases (Yaghi).

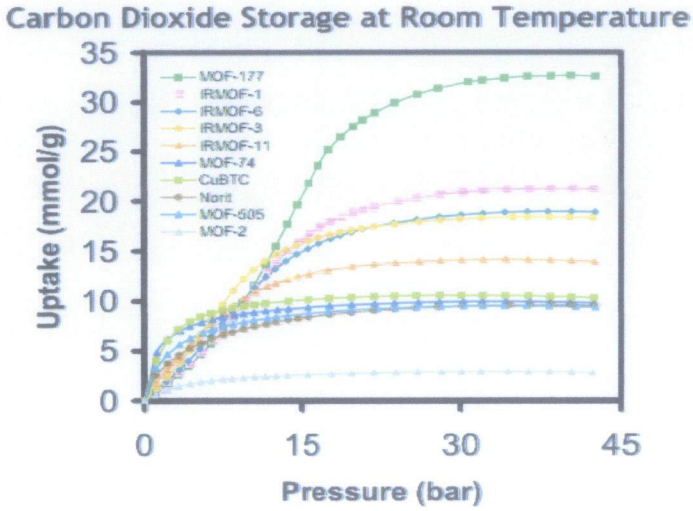


Figure 7: Carbon dioxide storage in different MOFs at room temperature.

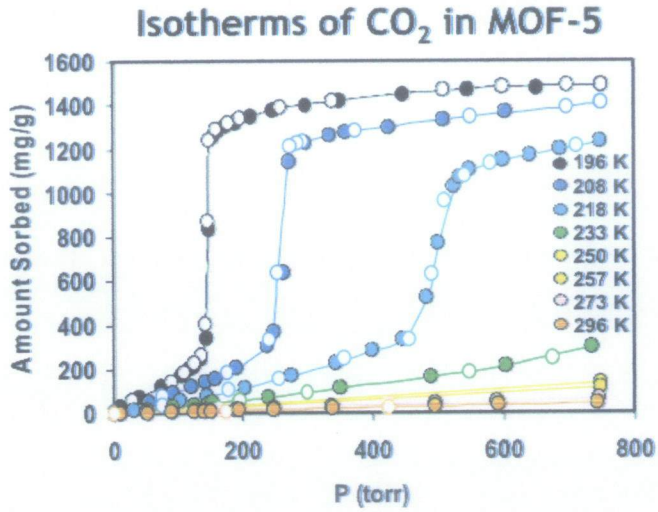


Figure 8: Adsorption of CO_2 in MOF-5

According to Yang et al., MOF-5 is a potential gas storage medium as it is one of the most thermostable, has the highest porosity and high H_2 capacity among the reported MOFs. However, at the temperature of 298 K, MOF-5 shows low H_2 storage capacity and it is very sensitive towards water even under atmospheric conditions where it shows a sharp reduction in surface area after prolonged exposure to humid air (Yang et al., 2009).

2.4 Synthesis and Characterization of MOF-5

MOF-5 can be synthesized by using a few methods. The most popular method that has been used in synthesizing MOFs is solvothermal method where a mixture of organic linker and metal salt are heated in a solvent system, usually together with formamide. According to the original paper in 1999, MOF-5 was synthesized by using the diffusion of triethylamine into a solution of zinc(II) nitrate, benzene-1,4-dicarboxylic acid and hydrogen peroxide in N,N-dimethylformamide (DMF) (Telfer, 2010). From the synthesize, a large single crystals of MOF-5 can be produced with a high BET surface area up to 3400 m^2/g (Zhang & Hu, 2011).

Another method that had been used is synthesizing at the room temperature where the synthesis is done at ambient temperature only and no heating is required. The Langmuir surface area for the produced MOF-5 was found to be 3909 m^2/g. Other

than that, Yan et al. has developed a "direct mixing" method which is a fast method to synthesis nano MOF-5 at macroscopic quantity. Hydrogen peroxide (H_2O_2) and Amine are added into dimethylformamide (DMF) solution of zinc nitrate and 1,4-benzenedicarboxylic acid (H_2BDC) at room temperature. Macroscopic quantity of porous nano-crystals can be produced in an hour with diameter of 30–150 nm. The surface area of the produced nano MOF-5, however is relatively small (in range of 300–1000 m^2/g) (Zhang & Hu, 2011). Recently, MOF-5 layers are reported that it can be synthesized by microwave heating where the porous alumina substrate is coated with conductive layer. Then, in a very short period of time, MOF-5 crystals could selectively form on the coated surface (Y. Liu et al., 2009).

Most of the MOF samples were characterized by using Brunauer-Emmet-Teller (BET), thermal gravimetric analysis (TGA), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and powder x-ray diffraction (XRD).

2.5 Modified MOF-5

MOF-5 structure can be modified by using other materials in order to enhance the performance. MOF-5 has low thermal conductivities, thus, limiting the performance of adsorption storage system (Purewal et al., 2012). According to Liu et al., hydrogen stored amount can be maximize when the heat generated during the adsorption from the storage bed is being remove to reach the desired operating temperature quickly (D. Liu et al., 2011). In this study, two materials have been chosen as the modifying materials for MOF-5.

2.5.1 Multi Wall Carbon Nanotubes (MWCNTs)

MWCNTs has been studies as composite fillers in various applications to enhanced the composite performance. The performance can be enhanced because of the unusual electroconductive, thermoconductive, mechanical and hydrophobicity properties of the CNTs. Yang et al. had successfully modified CNT@MOF-5 and found that H_2 storage capacity at room temperature has been improved and moisture stability can be increased (Yang et al., 2009). On the other hand, Park and Yi had

also proven that the presences of CNTs in MOF-5 structure, influences the enhancement of hydrogen storage (Park & Lee, 2009).

2.5.2 Expandable Graphite

Expandable graphite is a form of intercalated graphite. It is also known as intumescent flake graphite or expandable flake. Usually, it is being used as an electrically conductive additive or as thermal transfer enhancement. A variety of metal and complex hydride storage materials $NaAlH_4$, La-Ni-Sn and $LaNi_5$ have successfully used small quantities of EG as thermal conductivity enhancers (D. Liu et al., 2011).

2.6 Summary of Literature Review

According to the literature review, there are many advantages of using MOFs especially as the gas storage or gas separator. Compared to zeolites that typically have 700 m^2/g, MOFs can have much greater surface areas from 1000 to 4000 m^2/g. On the other hand, other functional groups can be introduced into the structure through ligands which means the structure can be easily modified to enhance the porosity. MOFs also do not have walls, like zeolites, to impede the diffusion of guest molecules.In this study, MOF-5 has been chosen as the main subject because as stated in the literature review, MOF-5 is one of the MOFs that has high surface area and high porosity compared to other MOF series. Furthermore, the raw materials are easily to be get and it is easy to be prepared.

CHAPTER 3

METHODOLOGY

In this project, the methodology is divided into three main parts. The divided parts are synthesis of MOF-5 and the modified MOF-5, characterization of the samples, and also CO_2 adsorption studies towards MOF-5, MWCNTs@MOF-5 and also EG@MOF-5.

3.1 Project Activities

3.1.1 Synthesis of MOF-5

MOF-5 is being synthesised by using solvothermal method. 1.071 g zinc nitrate hexahydrate and 0.198 g terephthalic acid is weighted and put in a small beaker seperately. Then, 30 mL of dimethylformamide (DMF) is added into both beakers and the solutions are mixed together. After zinc nitrate and terephtalic acid dissolved in DMF, another 120 mL DMF are added and the solutions are mixed together in a beaker. After that, the solution is put into a Teflon cylinder where the Teflon is then being put into an autoclave. The solution is heated in the oven at 105°C for 24 hours. When the autoclave is taken out from the oven, the crystals formed are washed with DMF and being centrifuge for three times. The crystals are then soaked into 20 mL chloroform. The chloroform is changed daily for three days. After that, the crystal is put in the vacuum oven for 24 hours with the temperature of 85°C and the pressure of 300 mbar.

The same method had been used to modify MOF-5 with multi wall carbon nanotubes (MWCNTs) and expandable graphite (EG). However, 0.04 g MWCNTs that had been dissolved in 40 mL DMF was mixed together with 0.714 g zinc nitrate, 0.132 g terephtalic acid and 120 mL DMF. For EG, 0.08 g EG that had been dissolved in 40 mL DMF was mixed together with 0.714 g zinc

nitrate, 0.132 g terephtalic acid and 120 mL DMF After that, the next method will be the same as the MOF-5 synthesis method.

The tools and apparatus used in this project are Teflon cylinder with autoclave as in Figure 9, drying oven, vacuum oven, centrifuge as in Figure 10, beakers, measuring cylinders, spatulas and pipette.

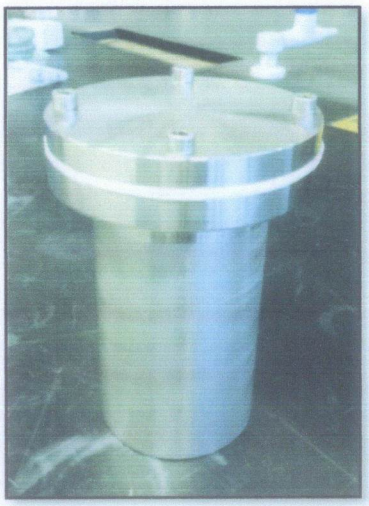


Figure 9: Teflon cylinder with autoclave

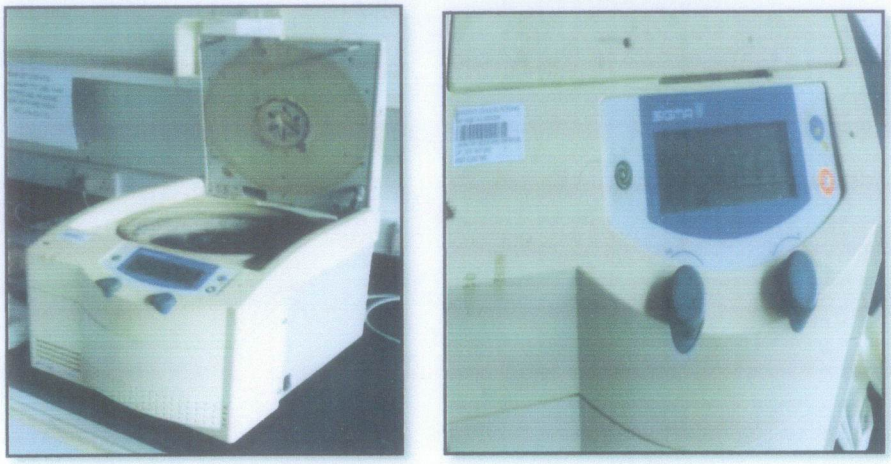


Figure 10: Centrifuge

3.1.2 Characterization of MOF-5

In this project, there are five characterization need to be made. First, characterization is made by using X-Ray Diffractometry (XRD) to determine the crystal structure and identify the single-phase materials, in this case, chemical compound of MOF-5. BET (Brunauer, Emmett and Teller) can evaluate the value of superficial specific surface area of the material by using the principle of the inert gas adsorption, usually nitrogen gas, to varying the relationship between the partial pressure of nitrogen and its vapour pressure to the temperature of liquid nitrogen.

On the other hand, the characterization can also be done by using Transmission Electron Microscopy (TEM) and Field Emission Scanning Electron Microscope (FE-SEM) where those instruments can analyse the samples morphology and surface texture. FESEM is an electron microscope that allows ultra-high resolution electron imaging up to x1,000,000 and 3 to 6 times better than conventional SEM. Meanwhile, TEM uses energetic electrons to produce high resolution, black and white images in the realms of microspace (1 μm) to nanospace (1nm), providing the morphology, compositional and crystallographic information on the samples. The difference of those instruments is TEM can produce two-dimensional images while FE-SEM can produce three-dimensional images.

Thermogravimetric analysis (TGA) is used to measure the weight gain or loss during a heating or cooling process. TGA thermal curve is displayed with the X-axis as the time or temperature and the Y-axis as the weight (mg) or the weight percent (%).

3.1.3 CO_2 Adsorption by Using MOF-5

CO_2 adsorption is being analysed by using BET Belsorp Mini II as in Figure 11 where it is a compact, volumetric instrument that used to analyse the specific surface area and pore distribution measurement. Before the samples are being

tested, they are heated in the drying oven for 2 hours and being weighted around 0.2 g. Then, the samples are being heated again for another one hours. To measure adsorption, the samples need to be pre-treated first. Then, the operation will be automatically carried out by the software starting with free space measurement. Then, it is followed by the adsorption and desorption measurement. This machine can reduce the possibility of human error, hence, increase the reliability and reproducing. The adsorption testing is conducted at the temperature of 298.15 K and pressure of 1 atm.

Figure 11: BET Belsorp Mini II

CHAPTER 4

RESULT AND DISCUSSION

4.1 Synthesis of MOF-5

After the synthesis of MOF-5 and MWCNTs at rate of MOF-5, the observation has been made. The quantity of MOF-5 and MWCNTs at rate of MOF-5 that can be synthesized by those methods is very low. Figure 12 shows the samples produced after the synthesis. Therefore, the synthesize method was being repeated for a few times in order to get enough amount of MOF-5 and MWCNTs@ MOF-5 to do characterization and experiment.

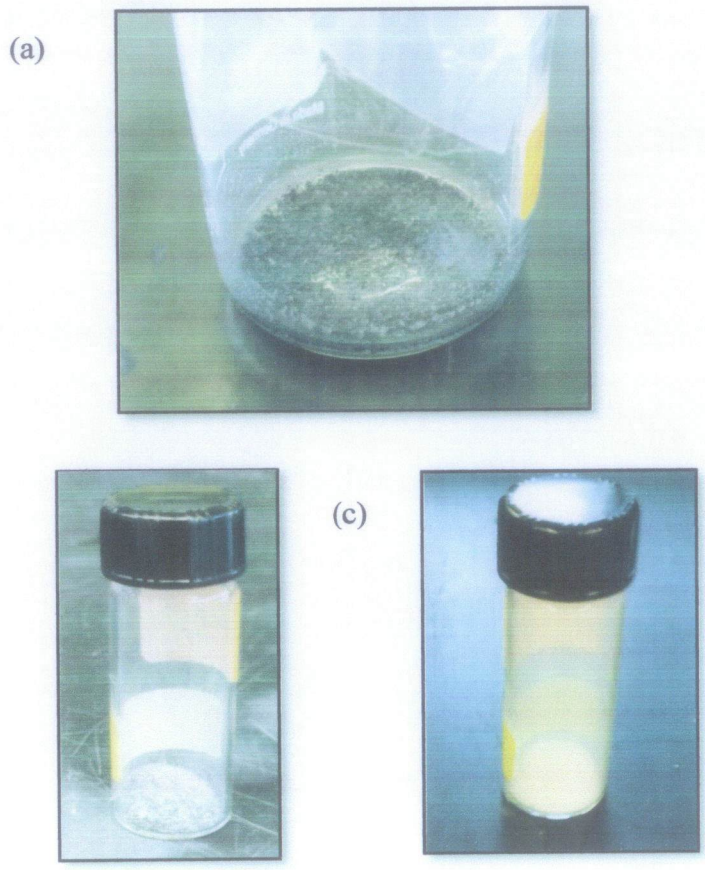


Figure 12: (a): MWCNTs@ MOF-5 before being dried in the vacuum oven. (b): MWCNTs@ MOF-5 after being dried in the vacuum oven. (c): MOF-5 after being dried in the vacuum oven.

During the synthesis process, the pores of the crystals are full of DMF (the solvent) molecules. When the crystals is being heated in the oven, the solvent molecules will be removed and leave the solid with accessible pore volume. The crystals are being centrifuge after heating in the oven in order to remove the unreacted particles.

4.2 Characterization

For the characterization, MOF-5 had been characterized by using TEM, FESEM, TGA, XRD and BET. However, since MWCNTs@ MOF-5 was synthesized a bit late than MOF-5, the characterization could only be made for XRD and BET.

4.2.1 XRD Analysis

Figure 14 shows the XRD patterns of MOF-5. Although the 2 theta (degree) are not the same but the peaks pattern are almost the same as in Figure 13 taken from the literature review by Cheng et al.

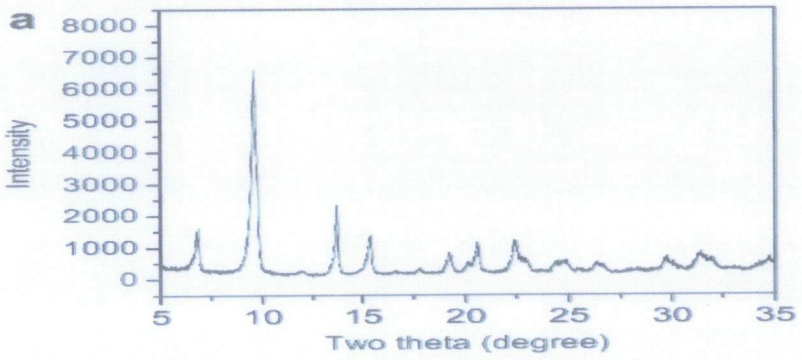


Figure 13: XRD Pattern for MOF-5 from the literature review (Cheng, Liu, Zhao, & Li, 2009)

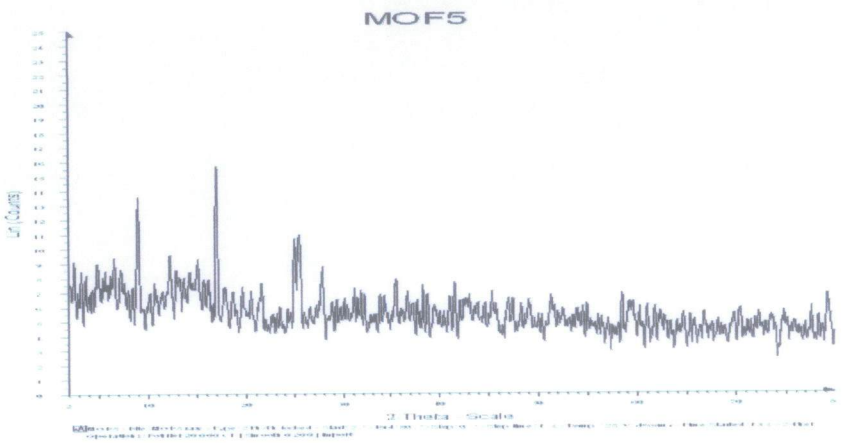


Figure 14: XRD Analysis of MOF-5

4.2.2 Surface Morphology

Figure 15 shows FESEM images of MOF-5 while Figure 16 shows TEM images of MOF-5.

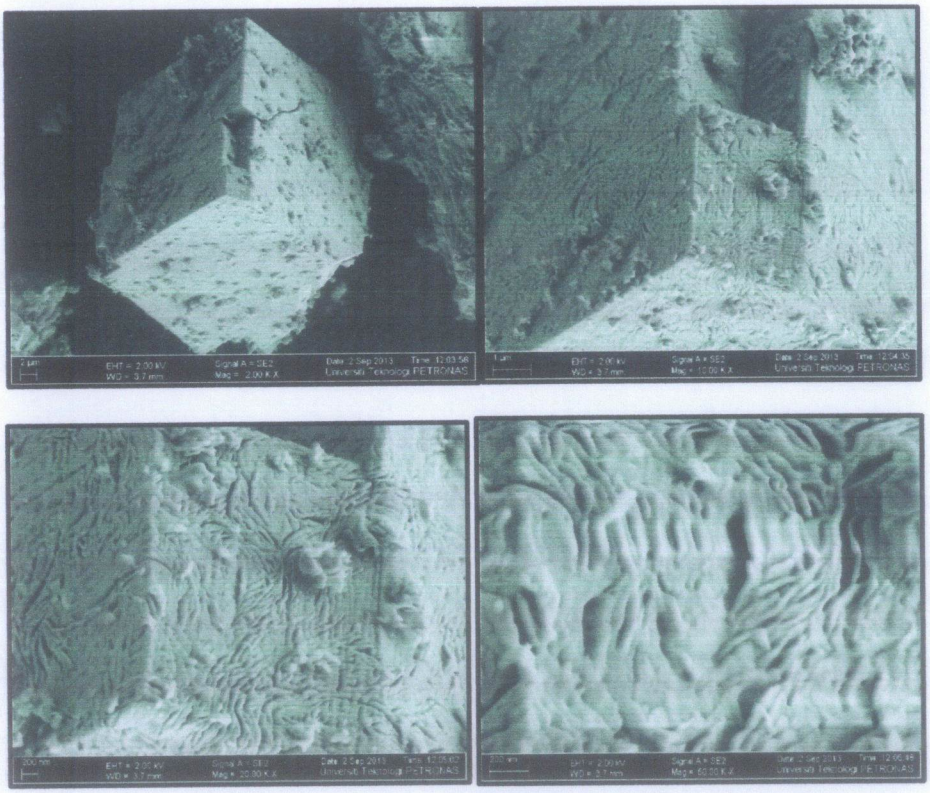


Figure 15: FESEM images of MOF-5.

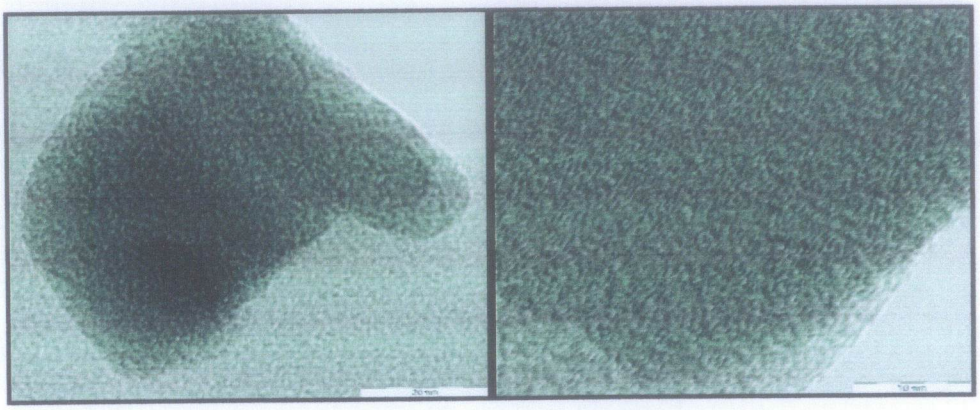


Figure 16: TEM images of MOF-5

The images from both analyses give the same result as in the literature review. The images show the cubic shape of the crystals and at high magnification, the images show pores on the surface of the crystals.

4.2.3 BET Surface Area

Figure 17 shows the graph of BET surface area plot for MOF-5 while Figure 18 shows the graph of BET surface area plot for MWCNTs@ MOF-5. More results show in Appendix 1 and Appendix 2.

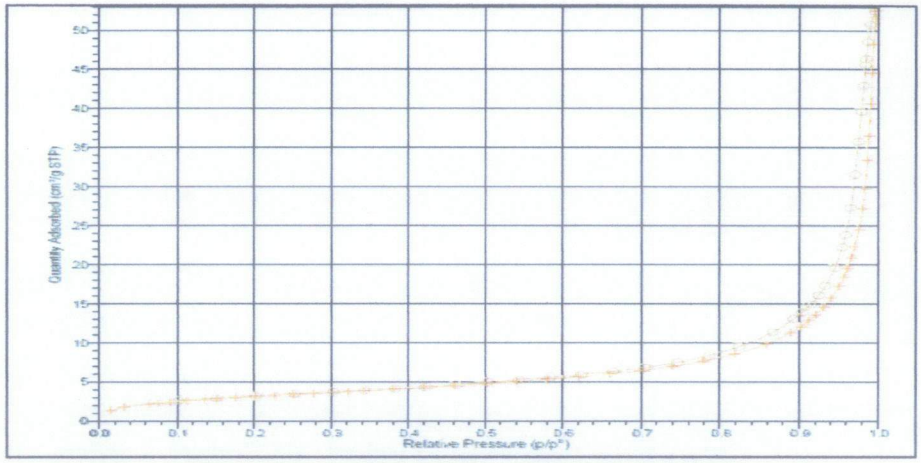


Figure 17: Isotherm Linear Plot for MOF-5

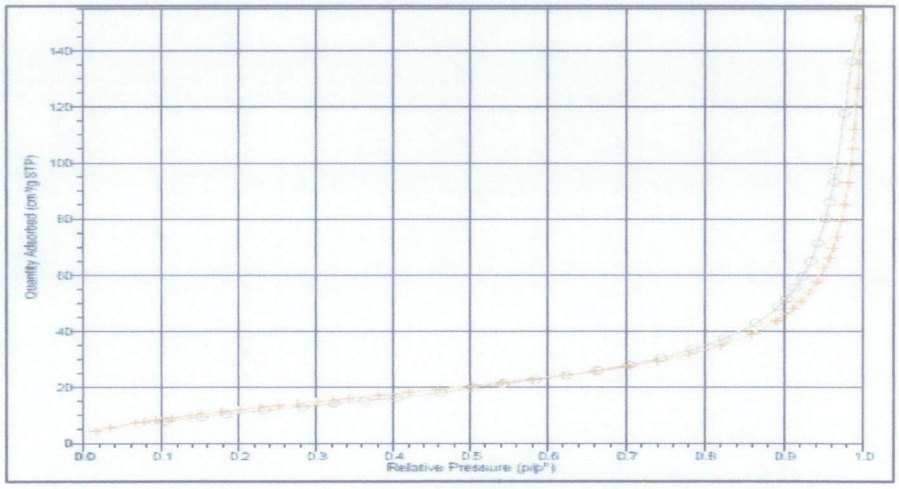


Figure 18: Isotherm Linear Plot for MWCNTs@ MOF-5

The BET analyses did not give a good result as the expected one. According to the literature review, MOF-5 should have BET surface area up to 3000 m^2/g. However, when the analyses were done for MOF-5 and MWCNT@ MOF-5, the results of BET surface areas are very small which are 11.6918 m^2/g and 50.0576 m^2/g respectively. Thus, the modified MWCNTs@MOF-5 will absorb more CO_2 than MOF-5 itself.

4.2.2 TGA Analysis

TGA analysis for MOF-5 is shown in Figure 19 which is a graph of weight% versus time. For the first 125 minutes, the graph shows some weight loss which is the loss of dimethylformamide (DMF). At 420th minutes, the weight% is loss drastically where it shows the loss of BDC (terephtalic acid) occurs and left with Zn_4O only.

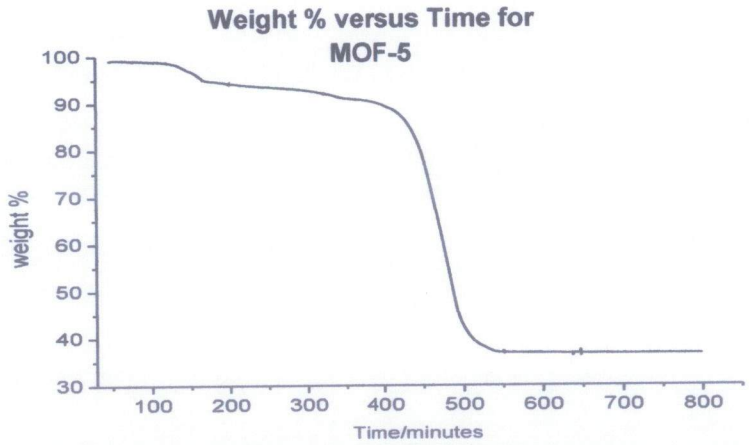


Figure 19: TGA analysis of MOF-5

MOF-5 structure is very sensitive to the moisture and water. Therefore, extra careful is needed when handling the samples as the samples should not be exposed to the air moisture. This might be one of the reasons why some of the characterization did not give good results as in the literature reviews.

4.3 CO_2 Adsorption Testing

The adsorption of CO_2 had been tested using BET machine. Table 1 shows the comparison of CO_2 adsorption of those three samples meanwhile Figure 20 illustrates the CO_2 adsorption isotherm graph of MOF-5, EG@MOF-5, MWCNTs@MOF-5. The raw graph of CO_2 adsorption performance can be referred to Appendix 3.

Table 1: CO_2 adsorption comparison in terms of mol/g between MOF-5, EG@MOF-5 and MWCNTs@MOF-5

MOF-5	
p/p_0	n_a/mol g^{-1}
0.053285	9.5846E-06
0.2259	3.4251E-05
0.4024	5.3703E-05
0.6032	7.0996E-05
0.8040	8.5875E-05
1.0044	9.9447E-05

EG@MOF-5	
p/p_0	n_a/mol g^{-1}
0.050417	7.9522E-06
0.215200	3.0629E-05
0.390400	5.2092E-05
0.541400	7.0269E-05
0.691300	8.8146E-05
0.841300	0.00010601
0.991200	0.00012414

MWCNTs@MOF-5	
p/p_0	n_a/mol g^{-1}
0.040942	3.3277E-05
0.2922	0.00019055
0.4203	0.00025178
0.5696	0.00031301
0.7217	0.00036756
0.8739	0.00041593
1.0254	0.00045994

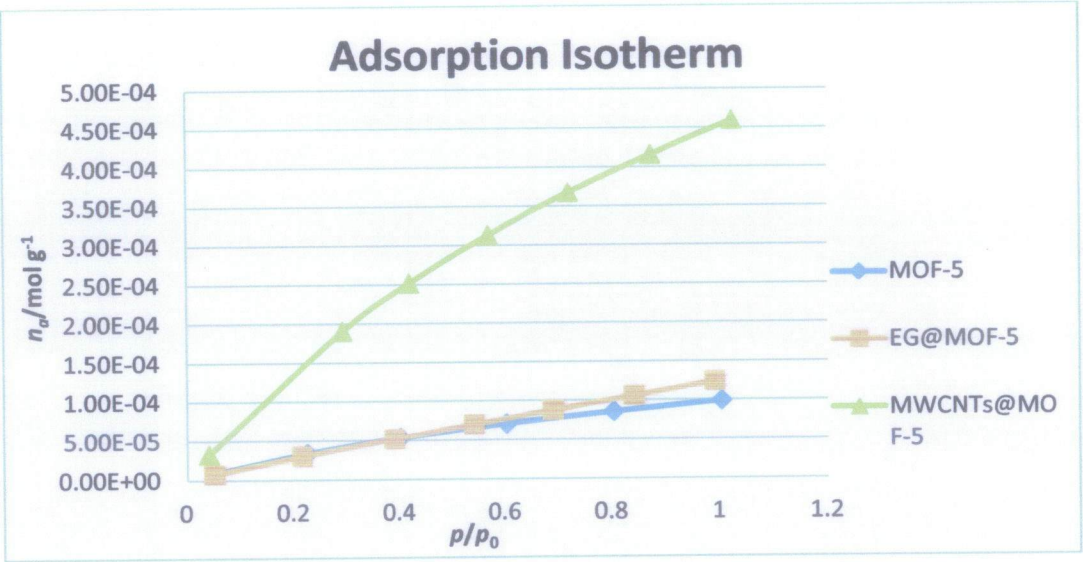


Figure 20: CO_2 adsorption and desorption isotherm graph of MOF-5, EG@MOF-5, MWCNTs@MOF-5.

The results found out that the CO_2 adsorption in the modified MOF-5 with MWCNTs give the highest value of adsorption in terms of mol CO_2 per gram adsorbent following by EG@MOF-5 and MOF-5. The performance of CO_2 adsorption in EG@MOF-5 and MOF-5 only shows a bit difference where EG@MOF-5 adsorbed slightly more than MOF-5 at the higher p/p_0. Thus, according to the results, the modified MOF-5 with MWCNTs can improve the adsorption of CO_2 and the porosity of the MOF-5 structure.

CHAPTER 5

CONCLUSION

For the past decade, thousands of MOF materials have been synthesized and characterized structurally. Yet, only a small part has been checked for CO_2 adsorption, storage, and related gas separation. In this final year project, MOF-5, EG@MOF-5 and MWCNTs@MOF-5 are successfully synthesized. XRD pattern shows similar result with the pattern in literature review. The images of FESEM and TEM show pores and the cubic structure of MOF-5. In addition, the TGA graph also the result similar to literature review. BET surface of the synthesized MWCNTs@MOF-5 is more than MOF-5 BET surface area. The modified MWCNTs@MOF-5 resulted in the highest CO_2 adsorption followed by the modified EG@MOF-5 and lastly, MOF-5. Thus, it can be concluded that the modified MWCNTs@MOF-5 adsorption can improve the performance of CO_2 adsorption and increase the porosity of MOF-5.

CHAPTER 6

RECOMMENDATION

There are some recommendations that can be made in the future. Even though MOF-5 is highly weak to water, but the crystalline structure of MOF-5 is stable in the ambient air without the presence of water vapor. As some of the characterization did not give exactly the same result as the expected result, more researches need to be done in order to study on the stability of MOF-5 structure in the ambient air with the presence of moisture. On the other hand, future research should also focus on modifying MOF-molecule to optimize the porosity and on the development of MOFs compatible with wider range of solvents, plus, allowing for shorter separation times.

REFERENCES

Caskey, S. (2009). Metal Organic Frameworks (MOFs). *Aldrich ChemFiles, 9*(2), 19.

Chae, H.K., Siberio-Perez, D.Y., Kim, J., Go, Y., Eddaoudi, M., Matzger, A.J., . . . Yaghi, O.M. (2004). A Route to High Surface Area, Porosity and Inclusion of Large Molecules in Crystals. *Nature, 427*(523).

Cheng, S., Liu, S., Zhao, Q., & Li, J. (2009). Improved synthesis and hydrogen storage of a microporous metal-organic framework material. *Energy Conversion and Management, 50*, 1314-1317.

Civalleri, B., Napoli, F., Noel, Y., Roetti, C., & Dovesi, R. (2006). Ab-initio Prediction of Materials Properties with CRYSTAL: MOF-5 as A Case Study. *CrystEngComm, 8*, 364-371.

Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M., & Yaghi, O.M. (2002). Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. *Science, 295*, 469.

Foundation, The Bellona (Producer). (2007). Retrieved from http://ebookbrowse.com/co2-capture-and-storage-pdf-d269254021

Jung, J.Y., Karadas, F., Zulfiqar, S., Deniz, E., Aparicio, S., Atilhan, M., . . . Han, S.M. (2013). Limitations and High Pressure Behavior of MOF-5 for CO_2 Capture. *Phys. Chem. Chem. Phys., 15*, 14319-14327.

Li, J.R., Ma, Y., McCarthy, M.C., Sculley, J, Yu, J., Jeong, H.K., . . . Zhou, H.C. (2011). Carbon Dioxide Capture-Related Gas Adsorption and Separation in Metal-Organic Frameworks. *Coordination Chemistry Reviews, 255*, 1791-1823.

Liu, D., Purewal, J.J., Yang, J., Sudik, A., Maurer, S., Mueller, U., . . . Siegel, D.J. (2011). MOF-5 composites exhibiting improved thermal conductivity. *International Journal of Hydrogen Energy, 37*, 6109-6117.

Liu, Y., Ng, Z., Khan, E.A., Jeong, H.K., Ching, C., & Lai, Z. (2009). Synthesis of continuous MOF-5 membranes on porous α-lumina substrates. *Microporous and Mesoporous Materials, 118*, 296-301.

Mu, B., Schoenecker, P.M., & Walton, K.S. (2010). Gas Adsorption Study on Mesoporous Metal-Organic UMCM-1. *The Journal of Physical Chemistry C., 114*, 6464-6471.

Park, S.J., & Lee, S. Y. (2009). Hydrogen storage behaviours of carbon nanotubes/Metal Organic Framework-5 hybrid composites. *Carbon Letters, 10*, 19-22.

Perez, E.V., Balkus, K.J., Ferraris, J.P., & Musselman, I.H. (2009). MIxed-Matrix Membranes Containing MOF-5 for Gas Separations. *Journal of Membrane Science, 328*, 165-173.

Purewal, J.J., Liu, D., Sudik, A., Veenstra, M., Yang, J., Maurer, S., . . . Siegel, D.J. (2012). Improved hydrogen storage and thermal conductivity in high-density MOF-5 composites. *The Journal of Physical Chemistry C., 116*, 20199-20212.

Saha, D., Bao, Z.B., Jia, F., & Deng, S.G. (2010). *Environ. Sci. Technol., 44*(1820).

Sciences, Carbon. (2012, 19 June 2012). CO2 Technology Could Dramatically Change the Economics of the Natural Gas Industry. 2013, from http://www.carbonsciences.com/view_news.php?id=122

Seki, K. (2001). Design of an Adsorbent with an Ideal Pore Structure Formenthane Adsorption Using Metal Complexes. *Chem. Commun.*, 1496.

Telfer, S.G. (2010). What Are These Things Called MOFs? *Chemistry in New Zealand*, 9-14.

Walton, K.S., Millward, A.R., Dubbeldam, D., Frost, H., Low, J.J., Yaghi, O.M., & Snurr, R.Q. (2007). Understanding Inflections and Steps in Carbon Dioxide Adsorption Isotherms in Metal-Organic Frameworks. *J. AM. CHEM. SOC., 130*, 406-407.

Yaghi, O.M.). Porous Crystals For Carbon Dioxide Storage. from http://www.netl.doe.gov/publications/proceedings/06/carbon-seq/Tech%20Session%20193.pdf

Yaghi, O.M., O'Keeffe, M., N.W., Ockwig., Chae, H.K., Eddaoudi, M., & Kim, J. (2003). Reticular synthesis and the design of new materials. *Nature, 423*, 705-714.

Yaghi, O.M., Rosi, N.L., Eckert, J., Eddaoudi, M., Vodak, D.T., Kim, J., & O'Keeffe, M. (2003). Hydrogen Storage in Microporous Metal-Organis Frameworks. *Science, 300*, 1127.

Yang, S.J., Choi, J.Y., Chae, H.K., Cho, J.H., Nahm, K.S., & Park, C.R. (2009). Preparation and Enhanced Hydrostability and Hydrogen Storage Capacity of CNT@MOF-5 Hybrid Composite. *Chem. Mater., 21*, 1893-1897.

Zhang, L., & Hu, Y.H. (2011). Observation of ZnO Nanoparticles Outside Pores of Nano $Zn_4O(C_8H_4O_4)_3$ Metal-Organic Framework. *Physics Letters A, 375*, 1514-1517.

APPENDICES

Appendix 1 – BET Surface Area for MOF-5

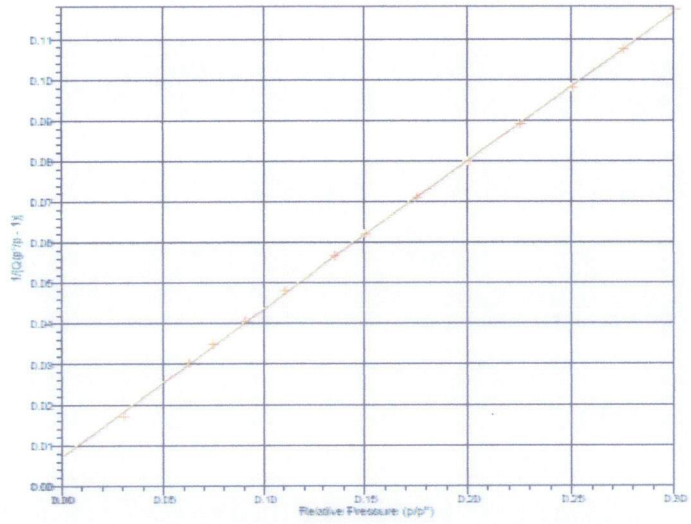


Figure 21: BET Surface Area Plot for MOF-5

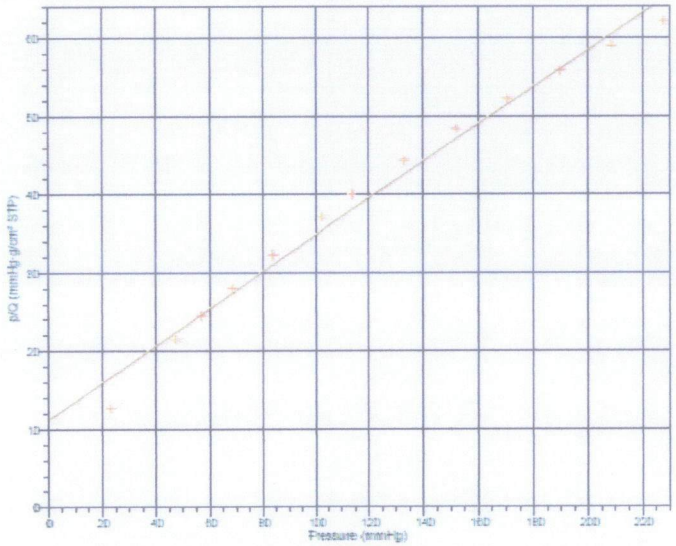


Figure 22: Langmuir Surface Area Plot for MOF-5

Appendix 2 – BET Surface Area for MWCNTs@MOF-5

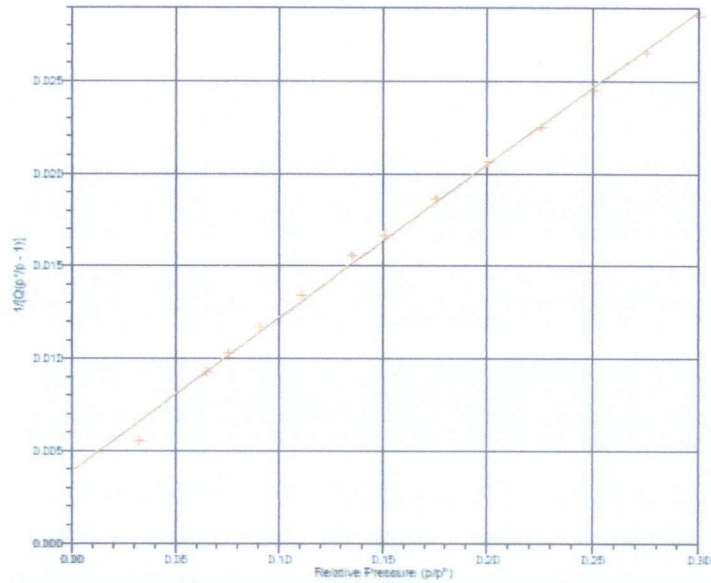


Figure 23: BET Surface Area Plot for MWCNTs@MOF-5

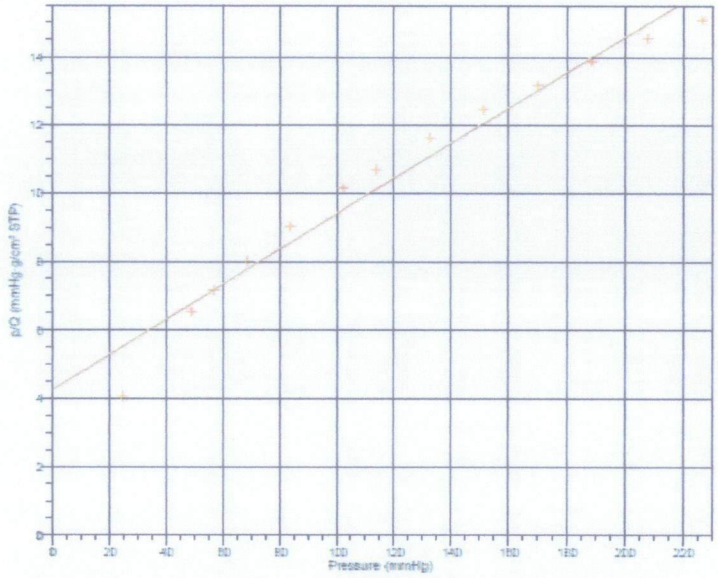
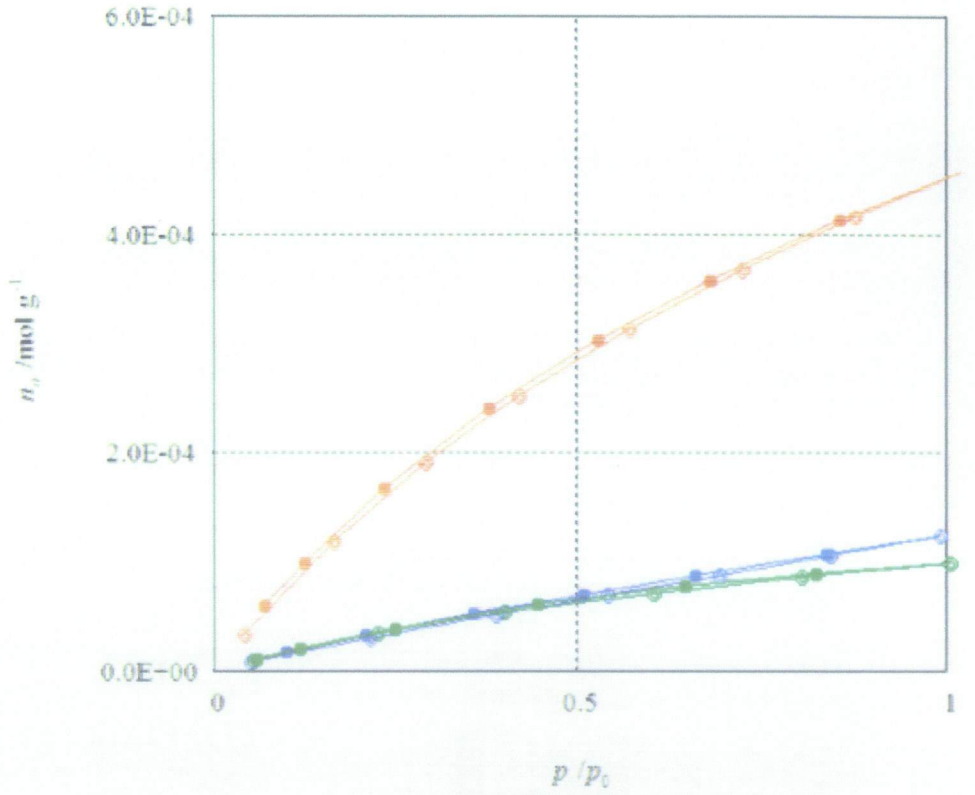


Figure 24: BET Surface Area Plot for MWCNTs@MOF-5

Appendix 3 – Adsorption/Desorption Isotherm



Adsorption / desorption isotherm

Filename COMMENT	Adsorptive	Adsorption temperature
MOF5@MWCNTs_CO2.DAT MOF5@MWCNTs_CO2	CO2	298.2
MOF5@EG_CO2.DAT MOF-5@EG_CO2	CO2	298.2
MOF-5_CO2.DAT MOF-5_CO2	CO2	298.2